Reactions of 1,3-Dihaloadamantanes with Carbanions in DMSO: Ring-Opening Reactions to Bicyclo[3.3.1]nonane Derivatives by the $S_{RN}1$ Mechanism

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The reactions of 1,3-dihaloadamantanes with various carbanionic nucleophiles were studied. Potassium enolates of acetophenone (**2**) and pinacolone (**10b**) and the anion of nitromethane (**10a**) reacted with 1,3-diiodoadamantane (**1a**) in DMSO under photostimulation by a free radical chain process to form a 1-iodo monosubstitution product as an intermediate, which undergoes concerted fragmentation to form derivatives of 7-methylidenebicyclo[3.3.1]nonene (**3** and **11**). This reaction does not occur in the dark at 25 °C, and the photostimulated reaction is partially inhibited by *p*-dinitrobenzene. 1,3-Dibromoadamantane (**1b**) and 1-bromo-3-chloroadamantane (**1c**) also reacted under irradiation with **2**, although more sluggish than **1a**, also giving the 7-methylidenebicyclo-[3.3.1]nonene derivative **3**. When a nucleophile was used without acidic hydrogens in the α-position, such as the enolate ion of isobutyrophenone (**16**), in order to inhibit the ring opening of adamantane, it reacted under irradiation with **1a** to give the products adamantane, 1-iodoadamantane, monosubstituted **17**, 1-iodo-monosubstituted **19**, and disubstituted **20**. Their distribution depended on the experimental conditions. In these reactions, 1-iodoadamantane and **19** were intermediates. For reactions involving the radical anion intermediate of the 1-iodo monosubstitution product, the intermolecular ET to the substrate was observed to be much faster than intramolecular ET to the C−I bond.

Several alkyl halides have been found to react with nucleophiles by the radical nucleophilic substitution, or $S_{RN}1$, mechanism.[1] The main steps that it involves are shown in eqs 1−3.

Initiation step:

$$RX + Nu^- \xrightarrow{ET} R^\bullet + X^- + Nu^\bullet \qquad (1)$$

Propagation steps:

$$R^\bullet + Nu^- \rightarrow (RNu)^{\bullet -} \qquad (2)$$

$$(RNu)^{\bullet -} + RX \rightarrow RNu + R^\bullet + X^- \qquad (3)$$

In the initiation step, when there is no spontaneous ET from the nucleophile to the substrate (eq 1), it can occur under photostimulation.[1] The alkyl radical thus formed couples with the nucleophile to give a radical anion (eq 2), which by an intermolecular dissociative ET[2] to the substrate yields the substitution product and the alkyl radical that continue the chain propagation steps (eq 3).

1-Haloadamantanes as well as other bridgehead halides react with nucleophiles by ET reactions.[1,3] The reactions of dihalo bridgehead compounds with nucleophiles give either the halo monosubstitution or disubstitution product depending on the radical type, the nature of the nucleofugal group, and the nucleophile.[4,5] The trimethylstannylation of dihalo bridgehead compounds in THF proceeds by a radical or polar process.[6]

The photostimulated reaction of 1,3-dihaloadamantanes with Ph_2P^- ions gave mainly the disubstitution product.[7] These substrates with $NaMe_3Sn$ in THF give products that depend on the leaving groups: with iodides or bromides the reaction proceeds predominantly with the formation of 1,3-dehydroadamantane, but with chlorides or 1-chloro-3-bromo, the disubstitution product is formed through the $S_{RN}1$ mechanism.[8]

1-Iodoadamantane reacted with carbanionic nucleophiles in DMSO under photostimulation[9] or was stimulated by $FeBr_2$ by the $S_{RN}1$ mechanism.[10] Taking this into account as well as the importance in synthesis of C−C bond formation, we undertook the investigation of the reactions of 1,3-dihaloadamantanes with carbanions in DMSO. We also studied the competition between intra- and intermolecular ET in the intermediate radical anion.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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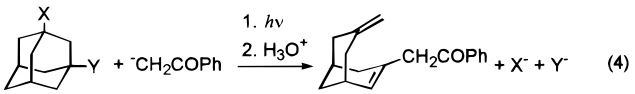
Table 1. Reactions of 1,3-Dihaloadamantanes 1 with 2 in DMSO

				product yields (%)	
expt	**1**, 10^2 M	**2**,[a] M	conditions	X^- [b]	**3**[c]
1	**1a**, 3.64	0.22	dark, 25 °C, 4 h	<3	
2	**1a**, 3.99	0.24	*hν*, 25 °C, 5 min	85	80
3	**1a**, 3.99	0.24	*hν*, 25 °C, 5 min[d]	25	26
4	**1a**, 0.50	0.03	*hν*, 30 °C, 5 min	87	83
5	**1a**, 4.02	0.24	dark, 60 °C, 3 h	93	88
6	**1a**, 4.00	0.24	dark, 60 °C, 3 h[d]	73	45
7	**1a**, 4.04	0.24	*hν*, 60 °C, 3 h	92	87
8	**1b**, 4.03	0.24	*hν*, 60 °C, 3 h	60	50
9	**1c**, 4.00	0.24	*hν*, 60 °C, 3 h	26[e]	21

[a] 0.28 M *t*-BuOK was added to form the carbanion **2** from acetophenone. [b] Considering two halide ions per molecule (determined potentiometrically). [c] Determined by GLC using $C_{24}H_{26}$ or Ph_3Sb as internal standard. [d] 20 mol % *p*-DNB was added. [e] 25% yield of chloride ions and 27% yield of bromide ions.

Results and Discussion

We found that there was no reaction of 1,3-diiodoadamantane (**1a**) with the enolate ion of acetophenone (**2**) at 25 °C in DMSO during 4 h (expt 1, Table 1). However, there is a very fast reaction with irradiation for 5 min under the same experimental conditions giving, through a ring-opening reaction, the monosubstitution product **3** (80%) after quenching. Although dehalogenation was extensive (85% based on two iodine ions per molecule of substrate) no disubstitution product was found (expt 2, Table 1) (eq 4). The photostimulated



(4)

1a: X = Y = I **2** **3**
1b: X = Y = Br
1c: X = Cl, Y = Br

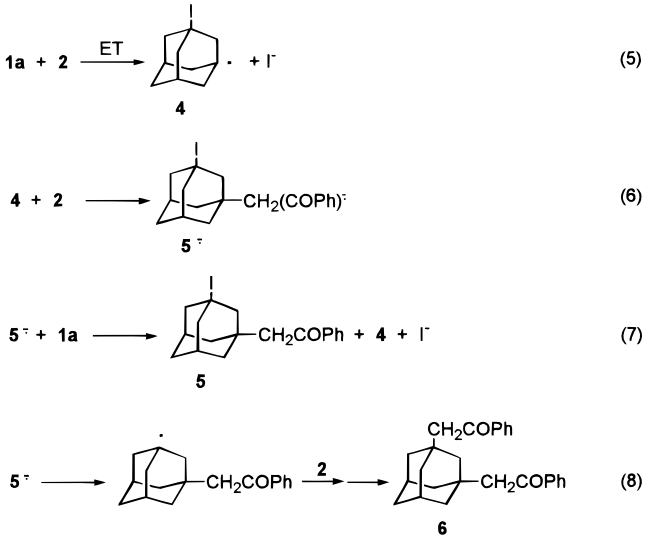
reaction was partially inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $S_{RN}1$ reactions, giving 26% of product **3** in the same period of time (expt 3, Table 1). The reaction was performed under dilute conditions in order to see if there was a change in the products, but only **3** (83%) was obtained again, and no disubstitution products were found (expt 4, Table 1).

Although there is no reaction at 25 °C during 4 h, at 60 °C in 3 h the reaction of **1a** with **2** yields **3** in 88% yield. This thermal reaction was also partially inhibited (45% yield of **3**) by *p*-DNB. On the other hand, there is no increase in the yield under irradiation (expts 5−7, Table 1).

These results can be explained according to the $S_{RN}1$ mechanism. The photostimulated or thermal ET from nucleophile **2** to the substrate **1a** gives the radical intermediate **4** and iodide ion (eq 5). This radical couples with **2** to give the radical anion intermediate $\mathbf{5}^{\bullet-}$ (eq 6). This radical anion intermediate which conceivably could undergo two competing reactions: intermolecular ET with the substrate **1a** to give **4** and **5** (eq 7), or intramolecular ET with the σ^* MO of the C−I bond, which by fragmentation would give a new radical intermediate. This in turn could couple with **2** leading finally to the disubstitution product **6** (eq 8) (Scheme 1).

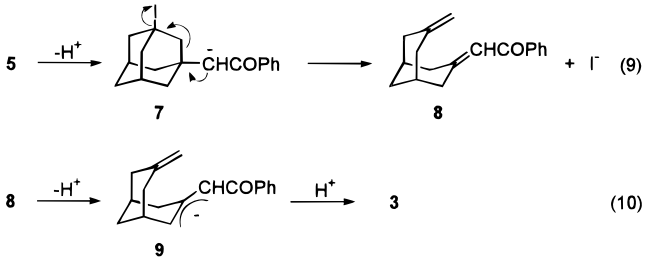
The fact that no disubstitution product **6** was formed indicates that intramolecular ET is too slow and does not compete with intermolecular ET. When the photostimulated reaction was carried out under more dilute conditions, and in order to increase the possibility of an intramolecular ET to give the disubstitution product **6**, only **3** was formed.

Scheme 1



These results differ from the results found in the photostimulated reaction of 1,3-dihaloadamantanes with Ph_2P^- ions in liquid ammonia, wherein all the substrates studied, even 1,3-dichloroadamantane, give mainly the disubstitution product and small amounts of the monosubstitution products. The halo monosubstitution product was not an intermediate in these reactions to give the disubstitution product.[7]

Since neither halo monosubstitution nor disubstitution products were found, it is suggested that the iodo monosubstitution product **5** is formed and is deprotonated under the basic reaction conditions to give the anion **7**, which by a ring-opening reaction renders the product **8** and iodide ions (eq 9). The product **8** is also deprotonated to give the carbanion **9**, and when the reaction is acidified, it gives the more stable isomer **3** (eq 10). There



are examples in the literature in which a substituent with acidic hydrogens, such as OH and SH, is present at C(1) of 3-bromoadamantane and concerted fragmentation to 7-methylidenebicyclo[3.3.1]nonane derivatives takes place under basic conditions.[11]

Since iodide ion is a very good leaving group, we switched to 1,3-dibromoadamantane (**1b**) to see if the ring-opening reaction is slow. In the photostimulated reaction of **1b** with **2** at 60 °C in 3 h, only **3** was found, together with 60% of bromide ions and **1b** (50%) (expt 8, Table 1). This reaction is slower than the reaction of **1a**,

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Table 2. Reactions of 1,3-Dihaloadamantanes 1 with 10a,b in DMSO

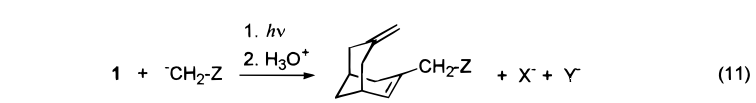
				product yields (%)	
expt	**1**, 10^2 M	**10**,[a] M	conditions	X^- [b]	**11**[c]
1	**1a**, 4.00	**10a**, 0.24	*hν*, 40 °C, 1.5 h	75	**11a**, 67
2	**1a**, 3.97	**10a**, 0.24	*hν*, 40 °C, 1.5 h[d]	10	**11a**, 11
3	**1a**, 4.00	**10a**, 0.24	*hν*, 40 °C, 1.5 h[e]	67	**11a**, 61
4	**1a**, 3.99	**10a**, 0.24	*hν*, 40 °C, 1.5 h[f]	83	**11a**, 55
5	**1a**, 3.99	**10a**, 0.24	dark, 60 °C, 3 h[f]	<5	**11a**,
6	**1b**, 4.00	**10a**, 0.24	*hν*, 60 °C, 3 h[f]	<5	**11a**,
7	**1c**, 4.07	**10a**, 0.20	*hν*, 60 °C, 3 h[f]	<5	**11a**,
8	**1a**, 3.97	**10b**, 0.24	*hν*, 30 °C, 5 min	86	**11b**, 80
9	**1a**, 3.98	**10b**, 0.24	*hν*, 30 °C, 5 min[d]	25	**11b**, 26
10	**1a**, 3.99	**10b**, 0.24	dark, 30 °C, 30 min	30	**11b**, 31
11	**1a**, 3.98	**10b**, 0.24	dark, 60 °C, 30 min	86	**11b**, 81
12	**1a**, 4.00	**10b**, 0.24	dark, 60 °C, 30 min[d]	85	**11b**, 80
13	**1a**, 0.50	**10b**, 0.03	*hν*, 30 °C, 5 min	87	**11b**, 80

[a] 0.28 M *t*-BuOK was added to form the carbanion **10a** or **10b** from nitromethane or pinacolone, respectively. [b] Considering two halide ions per molecule (determined potentiometrically). [c] Determined by GLC using 4-bromobiphenyl or phenanthrene as internal standards, respectively. [d] 20 mol % *p*-DNB was added. [e] 0.24 M *t*-BuOK was added to form the carbanion **10a** from nitromethane. [f] Acetone (0.08 M) and *t*-BuOK (0.36 M) were added.

in agreement with the higher electron affinity of iodo compounds compared to the corresponding bromo derivatives.[12]

The photostimulated reaction of 1-bromo-3-chloroadamantane (**1c**) is even more sluggish;[12] thus, in 3 h of irradiation only a 21% yield of **3** was obtained, with a 27% yield of bromide ions and a 25% yield of chloride ions. The substrate **1c** was recovered in high yield (expt 9, Table 1). These results suggest that the carbanion intermediates formed in these reactions rearranged very easily with iodide, bromide, or chloride ions as leaving groups at the 3-position of the adamantane ring.

We next studied the reaction of substrates **1** with a more stable and less basic nucleophile such as the nitromethane anion (**10a**) in order to see if the ring-opening reaction occurs with a more stable carbanion intermediate. 1-Iodoadamantane did not react with **10a** under irradiation in DMSO. However, the substitution product 1-adamantylnitromethane was obtained in 87% yield when the photostimulated reaction was performed in the presence of good electron donors such as acetone enolate ions (entrainment reaction).[9] However, we found that **1a** reacts under irradiation with **10a**, as expected by the higher electron affinity of **1a** compared with 1-iodoadamantane.[12] Thus, the photostimulated reaction of **1a** with **10a** in 1.5 h at 40 °C gives the rearranged product **11a** (61% yield). This reaction is inhibited by *p*-DNB (11% yield), and the yield is not increased with excess of *t*-BuOK or with the acetone enolate ion as an entrainment nucleophile. There was no reaction in the dark, even at 60 °C in 3 h (expts 1−5, Table 2) (eq 11).

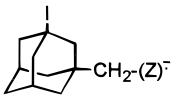


(11)

10a, Z = -NO_2 **11a**, Z = -NO_2
10b, Z = -$COCMe_3$ **11b**, Z = -$COCMe_3$

There was no photostimulated reaction with substrates **1b**,**c**, even in the presence of acetone enolate ions (expts 6 and 7, Table 2). All these results indicate that intermolecular ET to the substrate is much faster than intramolecular ET to the C−I bond, which would give the disubstitution product. With nucleophiles **2** and **10a**, the SOMO value of the radical anion intermediates, such as **5**$^{\bullet-}$ and **12a**$^{\bullet-}$, belongs to the benzoyl and nitro moieties[13] (Chart 1).

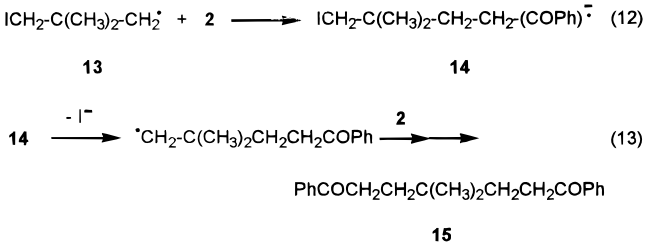
Chart 1



5$^{\bullet-}$, Z = COPh
12a$^{\bullet-}$, Z = NO_2
12b$^{\bullet-}$, Z = $COCMe_3$

In order to facilitate intramolecular ET to the C−I bond of the radical anion intermediate, formed when the carbanion couples with the 3-iodo-1-adamantyl radical (**4**), we studied the reaction of **1a** with pinacolone enolate ion (**10b**). In this case, the radical anion intermediate formed (**12b**$^{\bullet-}$) has the antibonding C−I bond lower in energy than the $-COCMe_3$ moiety and intramolecular ET is thermodynamically favorable. The photostimulated reaction between **1a** and **10b** is quite fast. In 5 min at 30 °C it gives an 80% yield of the rearranged product **11b** (eq 11). This photostimulated reaction is inhibited by *p*-DNB (26% yield of **11b**), and there is a reaction in the dark at 30 °C (31% yield of **11b**) that increases the yield to 81% at 60 °C. No unrearranged products were found under more dilute conditions to slow intermolecular ET (expts 8−13, Table 2).

The photostimulated reaction of 1,3-diiodo-2,2-dimethylpropane, a neopentyl type of structure with two leaving groups, with **2** gave the disubstitution product, and no products derived from the iodo monosubstitution product were formed.[14] These results indicate that the radical anion intermediate **14** formed in these reactions in the coupling of 3-iodo-2,2-dimethyl-1-propyl radical (**13**) with **2** has a very fast intramolecular ET to the C−I bond to give ultimately the disubstitution product **15** (eqs 12 and 13).



(12)

(13)

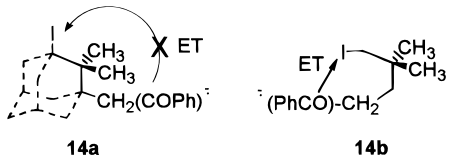
Although **14** has the same number of σ-bonds between the benzoyl radical anion and the C−I bond, the different rates of the intramolecular ET results can be explained on account of the rigid structure of the intermediate radical anions such as **5**$^{\bullet-}$ and **12**$^{\bullet-}$ in the adamantane system compared with the flexibility of the structure of the radical anion intermediate **14** in the neopentyl system. This radical anion can be a conformer similar

(12) The Ep vs SCE in acetonitrile are **1a**, −1.80 V; **1b**, −2.30 V; **1c**, −2.50 V; and 1-iodoadamantane, −2.20 V. Adcock, W.; Clark, C. I.; Houmam, A.; Krstic, A. R.; Pinson, J.; Savéant, J. M.; Taylor, D. K.; Taylor, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 4659.

(13) The SOMO values of **5**$^{\bullet-}$ (−1.99 eV) and **12a**$^{\bullet-}$ (−2.65 eV) belong to the benzoyl and nitro moieties, respectively, and are lower in energy than the σ^* values of the C−I bonds (2.66 and 2.88 eV, respectively). On the other hand, the SOMO value of radical anion **12b**$^{\bullet-}$ (−1.55 eV) belongs to the σ^* of the C−I bonds, the π^* of the carbonyl moiety being higher in energy. These calculations were carried out with the AM1 method.

(14) Peñéñory, A. B.; Rossi, R. A. *Gazz. Chim. Ital.* **1995**, *125*, 1.

Chart 2



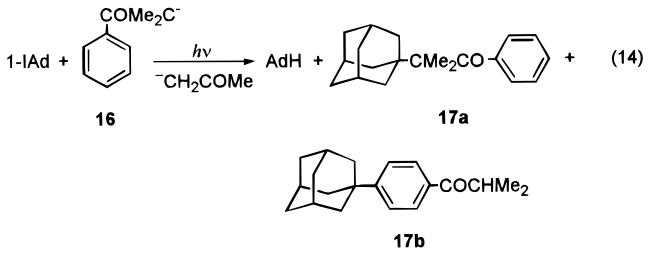
14a **14b**

to the adamantane **14a**, or due to the flexibility of this system, the benzoyl radical anion can be close to the C−I bond such as in **14b**, and from this type of conformer intramolecular ET is faster than in conformer **14a**. It seems therefore that intramolecular ET occurs through space and not through bonds because it should also occur in the adamantane system (Chart 2).

These results are in agreement with the γ-radiolysis of 1-benzoyl-ω-haloalkanes, which form the radical anion on the benzoyl moiety, and then by a unimolecular ET reaction to the C−X bond they form the radical. This ET reaction occurs through a cyclic transition state. With 1-benzoyl-4-iodobutane, a substrate that has the same amount of C atoms as **14** between the two reacting centers, the rate of ET is 6.0×10^7 in HMPA at 25 °C.[15]

The ring-opening reaction of the halo monosubstitution products formed in all these reactions occurs because of their acidic hydrogens in the α-position that give carbanions under basic reaction conditions. These, then, on losing the second halide ion in the 3-position of the adamantane, give the products through ring opening.

We studied the reaction of isobutyrophenone enolate ion (**16**), which after coupling with the radicals has no hydrogens in the α-position, with 1-iodoadamantane and **1a**. The photostimulated reaction of 1-iodoadamantane and **16** is sluggish, giving mainly the reduction product adamantane (AdH). When the reaction was performed under the same experimental conditions but in the presence of acetone enolate ion as an entrainment nucleophile, the products obtained were adamantane (35% yield) and the substitution products **17a** (6%) and **17b** (20%) together with small amounts of unknown products. When the reaction was performed in the presence of 18-crown-6 ether, there was a slight increase in the yield of products (AdH, 52%; **17a**, 6%; **17b**, 26%) (expts 1 and 2, Table 3) (eq 14). This reaction did not



occur in the dark, and the photostimulated reaction is inhibited by *p*-DNB, although some dehalogenation is observed (expts 3 and 4, Table 3).

It is known that when carbanions have hydrogens in the β-position, the reduction process competes with the coupling process.[16] Carbanion **16** has two methyl groups in the β-position, which facilitates the reduction process. The hydrogen abstraction by 1-adamantyl radical gives

(15) Kimura, N.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2433.

(16) Wolfe, J. F.; Moon, M. P.; Sleevi, M. C.; Bunnett, J. F.; Bard, R. R. *J. Org. Chem.* **1978**, *43*, 1019.

Table 3. Reactions of 1-Iodoadamantane with Isobutyrophenone Enolate Ion (16) in DMSO[a]

		product yields[b] (%)			
expt	conditions	I^-	**17a**	**17b**	adamantane
1	*hν*, 50 °C, 2 h	83	6	20	35
2	*hν*, 40 °C, 1.5 h[c]	88	6	26	52
3	dark, 60 °C, 3 h	25			
4	*hν*, 60 °C, 3 h[d]	45	2	5	*e*

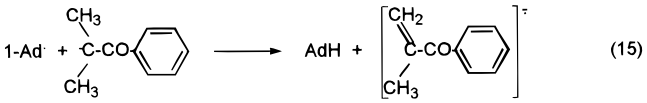
[a] 1-IAd (0.04 M), isobutyrophenone (0.13 M), acetone (0.05 M), and *t*-BuOK (0.18 M). [b] Adamantane was quantified with camphor as internal standard and **17** with Ph_4Sn; iodide ions determined potentiometrically. [c] 18-Crown-6-ether was added (0.18 M). [d] 20 mol % *p*-DNB was added. [e] Not quantified.

Table 4. Reactions of 1a with 16 in DMSO[a]

		product yields[b] (%)					
expt	conditions	I^- [c]	1-IAd	**17a**	**17b**	**19**	**20**
1	*hν*, 25 °C, 5 min	106	40	19	1	28	<2
2	*hν*, 25 °C, 5 min[d]	125	42	28	<1	24	<1
3	*hν*, 25 °C, 5 min[e]	9	<1			<1	
4	*hν*, 60 °C, 1.5 h[d,f]	184	<1	36	13	<1	14
5	*hν*, 60 °C, 3 h	180	<2	22	15	2	10
6	*hν*, 60 °C, 3 h[e]	*g*	30	17	3	<1	
7	dark, 60 °C, 1.5 h[d]	90	38			37	

[a] **1a** (0.04 M), isobutyrophenone (0.24 M), acetone (0.04 M), and *t*-BuOK (0.36) M. [b] 1-IAd was quantified with 1-BrAd, and **17**, **19**, and **20** with Ph_4Sn as internal standard. [c] Considering two iodide ions per molecule (determined potentiometrically). [d] 18-Crown-6-ether was added (0.36 M). [e] 20 mol % *p*-DNB was added. [f] Adamantane was quantified in 18% yield. [g] Not quantified.

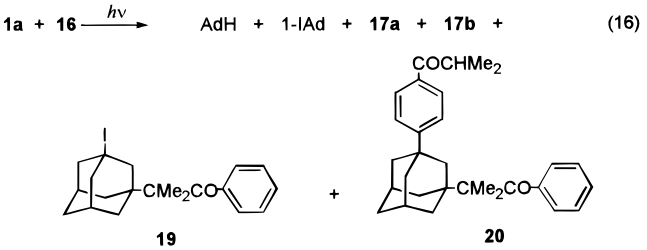
the radical anion of the unsaturated ketone **18**, which is able to propagate the chain process (eq 15). The fact that



16 **18**

the most important substitution product is the one formed by coupling in the *para*-position of the benzene ring suggests that this nucleophile is strongly sterically hindered.

The photostimulated reaction of **1a** with **16** gave a mixture of products, and the distribution depends on the irradiation time. At a short period of time (5 min) and at 25 °C, the main products obtained are 1-iodoadamantane (40%), the monosubstitution products **17a** (19%) and **17b** (1%), the iodo monosubstitution product **19** (28%), and the disubstitution product **20** (<2%) (expt 1, Table 4) (eq 16).



19 **20**

All the products found have the adamantane moiety, and no products through the ring-opening reactions were observed. The yields are slightly increased in the presence of 18-crown-6 ether, and the photostimulated reaction is inhibited by *p*-DNB (expts 1−3, Table 4).

When the photostimulated reaction is carried out at longer irradiation time (1.5 h) and at 60 °C, there is a

decrease in the yield of 1-iodoadamantane (<1%) and **19** (<1%) and an increase in the yields of the substitution products **17a** (36%) and **17b** (13%) and the disubstitution product **20** (14%). Similar results were found at a longer irradiation time (3 h). Under the same experimental conditions but with the addition of *p*-DNB, the yield of 1-iodoadamantane was 30%. In dark conditions and at 60 °C, there is a reaction that gives 1-iodoadamantane (38%) and **19** (37%) (expts 4−7, Table 4).

These results suggest that this is a stepwise reaction, with 1-iodoadamantane and **19** as intermediates, and the 3-iodoadamantyl radical intermediate (**4**) can either react with **16** by hydrogen atom abstraction to give 1-iodoadamantane as an intermediate or couple to give the radical anion $\mathbf{19}^{\bullet-}$ which renders ultimately product **19** by an intermolecular ET. At longer irradiation times and at an increased temperature, 1-iodoadamantane reacts with **16** to give adamantane and the monosubstitution products **17**. The iodo monosubstitution product **19** also reacts with **16** by hydrogen atom abstraction to give **17** or couples to give finally the disubstitution product **20**.

These results indicate that intramolecular ET of the radical anion intermediates to the C−I bond is much slower than intermolecular ET, similar to the behavior of the other carbanions studied here. The iodo monosubstitution product **19** has no β-hydrogens, and it is unable to undergo the ring-opening reaction. The adamantyl moiety is maintained in all the products found.

Experimental Section

General Methods. Irradiation was conducted in a reactor equipped with two 400-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water-refrigerated). Column chromatography was performed on silica gel (70−270 mesh ASTM). Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument with a flame-ionization detector and the data system Hewlett-Packard 3396 Series II, using a HP5 column (5% methyl silicone). Potentiometric titration on halide ions was performed in a pH meter (Seybold Wien), using an Ag/Ag^+ electrode and $AgNO_3$ as standard. HRMS were recorded at the Institute of Advanced Materials Study, Kyushu University, Japan, and LANAIS, Buenos Aires, Argentina.

Materials. 1-Bromoadamantane, 1-chloroadamantane, thionyl chloride, potassium *tert*-butoxide, silica gel (Aldrich Chemical Co.), hydriodic acid (Carlo Erba), phenanthrene, Ph_3Sb, 4-bromobiphenyl, *p*-dinitrobenzene (Fluka), chromic acid, and $C_{24}H_{26}$ were commercially available and used as received. Isobutyrophenone, pinacolone, nitromethane, acetophenone, and acetone were distilled and dried (molecular sieves, 4 Å). DMSO (Carlo Erba) was distilled under vacuum and stored over molecular sieves (4 Å).

Synthesis of 1,3-Dihaloadamantanes: Oxidation of 1-Haloadamantane and Halogenation of 3-Halo-1-adamantanol. The procedures were similar regardless of the starting material used. To a stirred solution of pulverized 1-chloroadamantane (or 1-bromoadamantane) (1.7 g, 10 mmol) in acetic acid and acetic anhydride (10 mL/10 mL) was added chromic acid (3 g, 30 mmol) over 60 min, and stirring was continued at room temperature for 24 h.[17] The residue was dissolved with water and then extracted with diethyl ether and methylene chloride. The combined organic extract was washed with a saturated $NaHCO_3$ aqueous solution and dried with $NaSO_4$ after removal of the solvents; 3-chloro-1-adamantanol was obtained which was then halogenated with hydriodic acid[18] to give 1,3-diiodoadamantane. Recrystallization from methanol gave the pure diiodide: mp 108−109 °C (lit.[19] mp 110−111 °C); ^{13}C NMR δ 33.6, 36.6, 44.5, 49.9, 64.3.

3-Bromoadamantanol was obtained from oxidation of 1-bromoadamantane and then was halogenated with thionyl chloride. 1-Bromo-3-chloroadamantane was isolated as a white solid after chromatography on silica gel (petroleum ether as eluant) and then sublimation: mp 100−101 °C (lit.[20] mp 101.5−103 °C).

In another experiment, 3-bromoadamantanol was halogenated with hydrobromic acid. The 1,3-dibromoadamantane was isolated as a white solid after chromatography on silica gel (petroleum ether as eluant) and then sublimation: mp 111−112 °C (lit.[21] mp 112−113 °C).

Photostimulated Reaction of 1,3-Dihaloadamantane with Acetophenone Enolate Ion (2) in DMSO. The following procedure is representative of all the reactions. Into a three-necked, 100-mL, round-bottomed flask equipped with a Liebig-West refrigerant, a nitrogen inlet, and a magnetic stirrer was added 25 mL of dry DMSO. *t*-BuOK (7 mmol) was then added followed by acetophenone (6 mmol) and the reaction mixture stirred for 10 min. The substrate (1 mmol) was then added and the mixture irradiated for 5 min. The reaction was quenched with addition of ammonium nitrate in excess and 50 mL of water, and then the mixture was extracted with diethyl ether. The products were quantified by GLC with the internal standard method. In another experiment the product was isolated as a white solid after chromatography on silica gel (petroleum ether−diethyl ether (95−5) as the eluant).

Photostimulated Reaction of 1,3-Dihaloadamantane with 2 in the Presence of *p*-DNB. The procedure was similar to that for the previous reaction, except that 20 mol % *p*-DNB was added to the solution of nucleophile prior to substrate addition.

α-(7-Methylidenebicyclo[3.3.1]non-2-en-1-yl)acetophenone, 3: ^{1}H NMR δ 2.4 (10 H, m), 3.7 (2 H, m), 4.5 (1 H, m), 4.7 (1 H, m), 5.7 (1 H, m), 7.6 (3 H, m), 8.0 (2 H, m); ^{13}C NMR δ 28.9, 30.8, 31.0, 35.6, 39.1, 42.6, 47.6, 110.9, 128.3, 128.7, 129.2, 132.7, 132.8, 136.9, 145.2, 196.9; MS (EI+) 51(3.0), 65(2.3), 77(58.1), 78(5.7), 79(4.2), 91(24.9), 92(6.7), 93(2.1), 105(100), 106(11.7), 107(2.9), 119(2.5), 132(7.1), 146(4.4), 197(9.3), 252(1.7); HRMS (EI+) calcd 252.1514, expt 252.1506.

α-(7-Methylidenebicyclo[3.3.1]non-2-en-1-yl)-nitromethane, 11a: ^{1}H NMR δ 2.15 (10 H, m), 4.5 (1 H, m), 4.7 (1 H, m), 4.8 (2 H, m), 5.9 (1 H, m); ^{13}C NMR 28.3, 30.3, 30.9, 33.3, 38.6, 42.7, 82.4, 111.7, 129.1, 136.3, 144.2; HRMS (EI+) calcd 193.1103, expt 193.1108.

α-(7-Methylidenebicyclo[3.3.1]non-2-en-1-yl)pinacolone, 11b: ^{1}H NMR δ 1.12 (9 H, s), 2.00 (10 H, m), 3.1 (2 H, m), 4.5 (1 H, m), 4.7 (1H, m), 5.4 (1 H, m); ^{13}C NMR δ 26.7, 27.0, 30.9, 31.2, 35.4, 39.2, 42.7, 44.6, 45.1, 110.7, 126.8, 132.6, 145.7, 213.8; MS (EI+) 41(10.7), 57(100), 58(4.9), 59(6.6), 69(6.9), 77(7.1), 79(9.4), 85(23.5), 91(38.8), 105(14.0), 107(6.6), 119(14.8), 132(10.3), 133(5.8), 135(5.7), 146(9.3), 147(9.5), 159(12.1), 177(3.7), 191(3.6), 232(5.3); HRMS (EI+) calcd 232.1827, expt 232.1829.

α-(3-Iodoadamant-1′-yl)isobutyrophenone, 19: ^{1}H NMR δ 1.25 (6 H, s), 1.85 (8 H, m), 2.52 (6 H, m), 7.40 (5 H, m); ^{13}C NMR δ 22.5, 32.9, 34.8, 35.7, 43.1, 50.8, 51.6, 51.9, 53.4, 127.2, 128.0, 130.2, 141.8, 211.4; MS (EI+) 43(3.7), 77(21.6), 91(15.2), 105(100), 106(16.3), 107(3.2), 119(5.2), 120(7.2), 121(2.4), 133(3.3), 134(3.5), 175(2.3), 176(4.2), 281(13.8), 283(3.4); HRMS (FAB+, matrix *p*-nitrobenzyl alcohol) calcd 409.1029 (M + 1), expt 409.1038.

α-(Adamant-1′-yl)isobutyrophenone, 17a: ^{1}H NMR δ 1.25 (6 H, d), 1.65 (6 H, m), 1.75 (6 H, m), 2.00 (3 H, m), 7.35 (3 H, m), 7.50 (2 H, m); ^{13}C NMR δ 22.4, 28.9, 37.0, 37.5, 38.0, 53.7, 127.4, 127.8, 129.9, 142.4, 212.2; MS (EI+) 41(6.4), 43(6.4), 55(11.2), 67(12.7), 77(24.2), 79(30.3), 81(20.1), 93(35.3), 95(15.2), 105(42.1), 121(19.1), 135(100), 136(11.3), 149(2.5), 176(16.4), 177(81.9), 178(11.9), 283(3.4); HRMS (EI+) calcd 282.1984, expt 282.1829.

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4-(Adamant-1′-yl)isobutyrophenone, 19b: ^{1}H NMR δ 1.21 (6 H, d, J = 6.8 Hz), 1.55−2.20 (15 H, m), 3.55 (1 H, sept, J = 6.8 Hz), 7.45 (2 H, d, J = 8.5 Hz), 7.91 (2 H, d, J = 8.5 Hz); ^{13}C NMR δ 19.2, 28.8, 35.2, 36.7, 42.9, 125.1, 128.3, 133.6, 156.5, 204.1; MS (EI+) 43(16.5), 55(7.0), 67(10.4), 79(24.2), 81(9.6), 91(25.7), 135(13.1), 154(6.7), 169(2.5), 239(100), 283(1.6); HRMS (FAB+, matrix *p*-nitrobenzyl alcohol) calcd 283.2061 (M + 1), expt 283.2065.

2-[3-(4-Isobutyrylphenyl)-1-adamantyl]-2-methyl-1-phenyl-1-propanone, 20: ^{1}H NMR δ 1.22 (6 H, d, J = 6.8 Hz), 1.27 (6 H, s), 1.79 (12 H, m), 2.24 (2 H, s), 3.55 (1 H, sept, J = 6.8 Hz), 7.44 (7 H, m), 7.91 (2 H, d, J = 8.5 Hz); ^{13}C NMR δ 19.2, 22.5, 29.2, 35.2, 35.9, 36.7, 37.5, 38.9, 42.1, 42.9, 53.7, 125.1, 127.3, 127.9, 128.4, 130.1, 133.8, 143.3, 155.9, 204.1, 211.9; MS (EI+) 323(100), 385(67), 428(17); HRMS (EI+) calcd 428.2716, expt 428.2716.

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Supporting Information Available: Spectral data for **3**, **11a,b**, **17a,b**, **19**, and **20** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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